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## Synthesis of Novel Symmetric Schiff Bases using KSF

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### ABSTRACT

Different novel symmetric Schiff bases were synthesized in a simple and environmentally benign method from the reaction of produced Schiff base with various aldehydes and ketones using montmorillonite KSF clay as heterogeneous solid acidic catalyst in good yields.

**Key words:** KSF; Hydrazine hydrate; bis Schiff base; terephthalaldehyde.

### INTRODUCTION

Schiff bases represent a class of important compounds in medicinal and pharmaceutical field. They have biological activities such as antibacterial<sup>1</sup>, anticancer<sup>2</sup>, antifungal<sup>3</sup>, and herbicidal activities<sup>4</sup>. Schiff bases have a chelating structure and are in demand because they are straightforward to prepare and are moderate electron donors with easily-tunable electronic and steric effects thus being versatile<sup>5</sup>.

Montmorillonite clays have been used as catalysts for a number of organic reactions and offer several advantages over classical acids: strong acidity, noncorrosive properties, recyclability, cheapness, mild reaction conditions, high yields and selectivity, and ease of setup and work up (6). Recently, we used montmorillonite KSF for synthesis of pyridazinones and phthalazinones<sup>7-9</sup>.

### EXPERIMENTAL

Melting points were measured on a Mettler Fp5 apparatus and are uncorrected. The IR spectra were recorded on a Shimadzu IR-470 spectrophotometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 500 MHz instrument using solvent as internal standard (CDCl<sub>3</sub> at 7.31 ppm and DMSO-d<sub>6</sub> at 2.50, 3.21 ppm). The UV-Vis spectra were recorded on Shimadzu UV-2100.

#### General procedure for the formation of compound 1

A solution of hydrazine hydrate (0.5 g, 10 mmol) in ethanol 5 mL was added dropwise to a stirred solution of terephthalaldehyde (0.67 g, 5 mmol) in ethanol 5 mL at room temperature. A yellow precipitate starts to form immediately upon addition; the stirring was continued for 1 hour. The

resulting solid was filtered and washed with EtOH to yield the desired compound.

#### **1,4-bis(hydrazonomethyl)benzene 1**

Yield 90%, m. p. 168 °C, yellow solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3350, 3200, 3050, 2900, 1630, 1590, 830.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.60 (s, 4H), 7.57 (s, 4H), 7.77 (s, 2H).  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 111.39, 126.79, 142.96. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 334.5.

#### **General procedure for the formation of compound 2a-3j**

Compound **1** (0.16 g, 1 mmol) and related aldehydes or ketones (2 mmol) was added in ethanol 10 ml. This mixture was heated to reflux in the presence of KSF (20 mg) for required time (4-8 hours). During the reaction a precipitate forms which is insoluble in the reaction solvent. After completion of the reaction, the mixture was allowed to cool to room temperature, then filtered, washed with EtOH and dried; recrystallization from DMF afforded the pure product.

#### **1,4-bis(((4-nitrobenzylidene) hydrazono) methyl)benzene 2a**

Yield 70%, m. p. > 310 °C, yellow solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3100, 2920, 1620, 1590, 1520, 1340, 830.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 7.72 (d, 4H,  $J = 8.9$  Hz), 8.02 (s, 4H), 8.25 (d, 4H,  $J = 8.84$ ), 8.71 (s, 2H), 8.76 (s, 2H). Anal. Calcd for  $\text{C}_{22}\text{H}_{16}\text{N}_6\text{O}_4$ ; C, 61.68; H, 3.76; N, 19.62; O, 14.94; found; C, 61.72; H, 3.74; N, 19.58; O, 14.95. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 347.5.

#### **1,4-bis(((3-nitrobenzylidene) hydrazono)methyl)benzene 2b**

Yield 73%, m. p. 230-236 °C, orange solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3100, 2920, 1620, 1520, 1350, 830, 730, 670.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 7.71 (m, 2H), 8.02 (s, 4H), 8.22 (d, 2H,  $J = 7.4$  Hz), 8.38 (d, 2H,  $J = 7.11$ ), 8.77 (d, 6H,  $J = 7.51$  Hz). Anal. Calcd for  $\text{C}_{22}\text{H}_{16}\text{N}_6\text{O}_4$ ; C, 61.68; H, 3.76; N, 19.62; O, 14.94; found C, 61.65; H, 3.90; N, 19.65; O, 14.91. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 348.5.

#### **1,4-bis(((2-hydroxybenzylidene)hydrazono) methyl)benzene 2c**

Yield 65%, m. p. 298-300 °C, yellow solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3350, 2900, 1620, 1590, 1450,

1210, 830.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 7.02 (t, 2H,  $J = 6.8$  Hz), 7.08 (d, 2H,  $J = 7.5$  Hz), 7.43 (m, 4H), 7.99 (s, 4H), 8.71 (s, 2H), 8.76 (s, 2H), 8.86 (s, 2H). Anal. Calcd for  $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2$ ; C, 71.34; H, 4.90; N, 15.13; O, 8.64; found C, 71.30; H, 4.94; N, 15.11; O, 8.66. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 375.2.

#### **1,4-bis(((3-hydroxybenzylidene) hydrazono) methyl)benzene 2d**

Yield 69%, m. p. decomposed at > 300 °C, orange solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3380, 2950, 1620, 1590, 1450, 1210, 830, 780, 680.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 500 MHz)  $\delta$ : 6.94 (s, 2H), 7.33 (s, 2H), 8 (s, 4H), 8.62 (s, 2H), 8.72 (s, 2H), 8.81 (s, 2H), 9.72 (s, 2H). Anal. Calcd for;  $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2$ ; C, 71.34; H, 4.90; N, 15.13; O, 8.64; found C, 71.31; H, 4.93; N, 15.11; O, 8.67. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 359, 323.5.

#### **1,4-bis(((4-methoxybenzylidene) hydrazono) methyl)benzene 2e**

Yield 64%, m. p. 210-214 °C, yellow solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2900, 2850, 1620, 1590, 1550, 1500, 1460, 1440, 1250, 1020, 830.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 3.9 (s, 6H), 7.49 (d, 4H,  $J = 5.8$  Hz), 8 (m, 8H), 8.51 (s, 2H), 8.76 (s, 2H). Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_2$ ; C, 72.34; H, 5.57; N, 14.06; O, 8.03; found C, 72.31, H, 5.61, N, 14.09, O, 8.01. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 369.2, 358.8.

#### **1,4-bis(((2-hydroxy,3-methoxybenzylidene) hydrazono) methyl)benzene 2f**

Yield 70%, m. p. 272-275 °C, orange solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3400, 2900, 1620, 1560, 1460, 1260, 1270, 830, 740.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 3.98 (s, 6H), 6.95 (t, 2H,  $J = 7$  Hz), 7.04 (d, 4H,  $J = 6.39$  Hz), 7.99 (s, 4H), 8.68 (s, 2H), 8.75 (s, 2H), 8.84 (s, 2H). Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_4$ ; C, 66.97; H, 5.15; N, 13.02; O, 14.87; found C, 66.99; H, 5.12; N, 13.05; O, 14.89. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 363.5.

#### **1,4-bis(((1-phenylethylidene) hydrazono)methyl)benzene 3g**

Yield 55%, m. p. 258-262 °C, yellow solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3050, 2920, 1620, 1560, 1440, 1360, 830, 760, 680.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 3.92 (s, 6H), 7.02 (m, 6H), 7.86 (d, 4H,  $J = 7.1$  Hz), 7.95 (s, 4H), 8.73 (s, 2H). Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_4$ ; C, 78.66; H, 6.05; N, 15.29; found C, 78.69; H, 6.07; N, 15.26. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 359.

**1,4-bis(((1-(4-methoxyphenyl)ethylidene)hydrazono)methyl)benzene 3h**

Yield 56%, m. p. > 300 °C, orange solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2920, 1620, 1540, 1500, 1250, 1030, 830.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 2.58 (s, 6H), 3.85 (s, 6H), 6.99 (d, 4H,  $J = 8.1$  Hz), 7.94 (s, 4H), 8.04 (s, 4H), 8.7 (s, 2H). Anal. Calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_2$  C, 73.22; H, 6.14; N, 13.14; O, 7.50; found C, 73.19; H, 6.16; N, 13.17; O, 7.48. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 373.5.

**1,4-bis(((1-(4-nitrophenyl)ethylidene)hydrazono)methyl)benzene 3i**

Yield 62%, m. p. 238-240 °C, yellow solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2900, 1620, 1590, 1510, 1340, 850, 830.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 2.54 (s, 6H), 7.94 (s, 4H), 8.09 (d, 4H,  $J = 8.8$  Hz), 8.27 (d, 4H,  $J = 8.8$  Hz), 8.71 (s, 2H). Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_6\text{O}_4$  C, 63.15; H, 4.42; N, 18.41; O, 14.02; found C, 63.17; H, 4.40; N, 18.43; O, 14.05. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 357.5.

**1,4-bis(((1-(4-hydroxyphenyl)ethylidene)hydrazono)methyl)benzene 3j**

Yield 55%, m. p. decomposed at > 240 °C, orange solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3400, 2900, 1620, 1560, 1440, 1210, 830.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 2.4 (s, 6H), 6.83 (d, 4H,  $J = 9$  Hz), 7.79 (d, 4H,  $J = 8.6$  Hz), 7.94 (s, 4H), 8.66 (s, 2H). Anal. Calcd for

$\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_2$  C, 72.34; H, 5.57; N, 14.06; O, 8.03; found C, 72.31; H, 5.59; N, 14.08; O, 8.01. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 357.5.

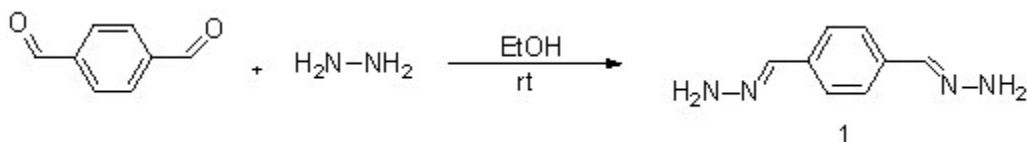
**General procedure for the formation of complex 4**

$\text{Cu}(\text{OAc})_2$  (1mmol) was added to a hot solution of the ligand **2c** (1mmol) in ethanol (10 ml) containing a few drops of TEA and the resulting mixture was refluxed for 3h. A pale green precipitate separated, which was collected by filtration and washed with ethanol. Yield 55%, m. p., pale green solid. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 1610, 1530, 1460, 1440, 1320, 1200, 1140, 960, 900. 820,740. Anal. Calcd for  $\text{C}_{44}\text{H}_{32}\text{Cu}_2\text{N}_8\text{O}_4$  C, 61.17; H, 3.73; Cu, 14.71; N, 12.97; O, 7.41; found C, 61.14; H, 3.74; Cu, 14.73; N, 12.6; O, 7.2. UV-Vis (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ) 284, 398.5.

**RESULTS AND DISCUSSION**

In contribution, to this Schiff bases synthesis, we first synthesized the one pot Schiff base **1** by reaction of terephthalaldehyde with hydrazine hydrate (Scheme 1) the reaction was completed in the short time and in good yield.

The next step was synthesis of the final Schiff bases by reaction of synthesized amine **1** utilizing different aldehydes and ketones (Scheme

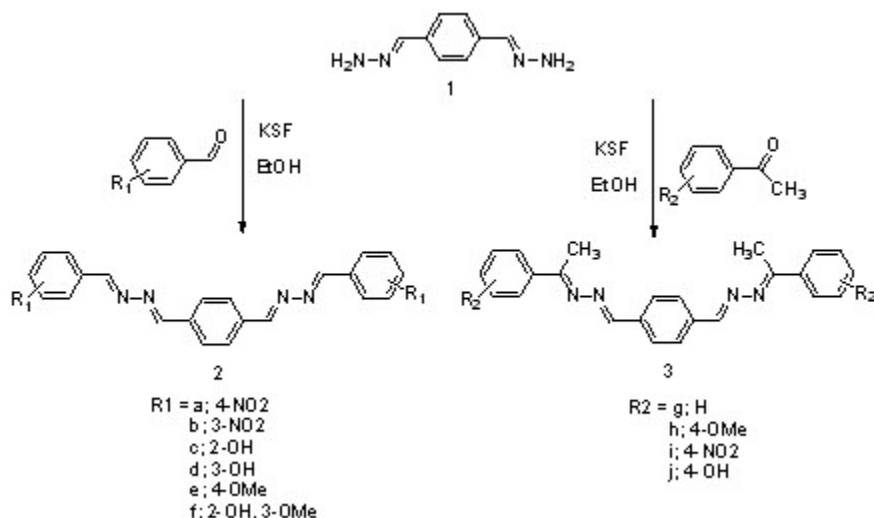
**Scheme 1: Preparation of imine 1**

2). In this reaction aldehydes react faster than ketones and the nature of the substituents on the aromatic ring of the aldehydes and ketones has different influences on the reaction rate. For instance, in the case of electron withdrawing groups such as nitro **2a** gives high yield of the products compared to those of the other substituents such as **2b-3j**.

Synthesis of the final products **2a-2f** and **3g-3j**, in the absence of montmorillonite KSF either failed or completed in a long reaction time together

with several byproducts. Performing a reaction in the presence of con. HCl as a catalyst due to conversion of some of the amine to its related hydrochloride salt gave only a tiny amount of mixture of salty products. While, we substitute montmorillonite KSF clay as a solid catalyst instead of the con. HCl surprisingly we covered a good yield of the final Schiff base products.

The UV-Vis spectra of compounds **2a-2f** and **3g-3j** compare to the UV-Vis spectra of the initial imine **1** have been recorded in the DMF solvent in



**Scheme 2: Preparation of final imines 2a-2f and 3g-3j**

the wavelength rang 800-250 nm (Fig. 1 & 2 Table 1). Figure 1 & 2 indicate that the products 2a-2f and 3g-3j compare to the initial imine 1 ( $\lambda_{\text{max}} = 334.5$ ) except to the 2d that shifted to the blue the other compounds all are shifted to the red field. This red shift are attributed to the long rang  $\pi \rightarrow \pi^*$  transitions of the respective compounds in the UV region. Absorption spectra of the prepared Schiff bases,

with various electron donating and withdrawing abilities, in DMF, are shown in Fig. 1. It can be found that when introducing the nitro group in the aryl component of the Schiff base, 2a and 2c, the absorption spectra give a remarkable less red shift than others. Compound 2a which has nitro group in para position compared to meta 2b nitro group, the absorption spectra give a remarkable red shift.

**Table 1: Results of spectroscopic studies in DMF as solvent**

Product	1	2a	2b	2c	2d	2e	2f	3g	3h	3i	3j
$\lambda_{\text{max}}$	334.5	347.4	348.5	375.2	359, 323.5	369.2, 358.8	363.5	359	373.5	357.5	357.5

The UV-Vis spectra of compounds 2e, 3h in three different organic solvents with different polarities (Fig. 3) reveal that the positions of the bands are influenced by the polarity of the solvents for 2e in DMF with highest polarity ( $\lambda_{\text{max}}/ 369.2$  nm), in a nonpolar solvent,  $\text{CHCl}_3$  ( $\lambda_{\text{max}}/ 358$  nm) and in EtOAc ( $\lambda_{\text{max}}/ 354.8$  nm) respectively were recorded. This solvchromic effect is attributed to the polarity of the solvents. In contrast to 2e, the 3h indicate a different absorption in  $\text{CHCl}_3$  ( $\lambda_{\text{max}}/ 370.4$  nm), in DMF ( $\lambda_{\text{max}}/ 358$  nm) and EtOAc ( $\lambda_{\text{max}}/ 359.2$  nm) respectively was recorded.

#### The reaction of copper (II) acetate salt with the Schiff base 2c yields crystalline complex 4

In the IR spectrum of compound 2c, a broad band observed in the region  $3400-3100 \text{ cm}^{-1}$  can be assigned to the  $\nu(\text{-OH})$  group. The absence of OH stretching band absorption in the IR spectra of complex 4 indicating that the oxygen atom is coordination to the copper (II) ion. In the other hand, the photometric study of the complex 4 indicate a ratio of ligand to copper ion as to be 1:1 this stoichiometric ratio allowed us to proposed the depicted structure (Scheme 3).

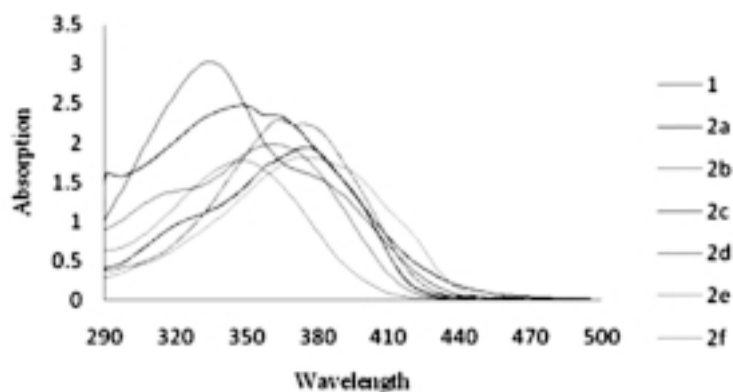


Fig. 1: Absorption spectra of compounds 2as-2f in DMF

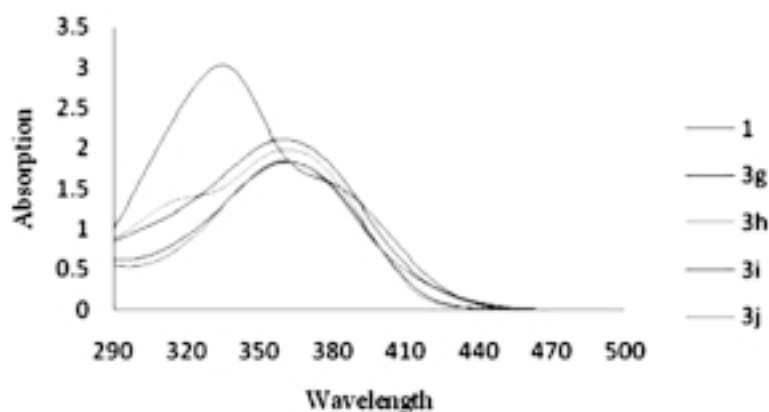


Fig. 2: Absorption spectra of compounds 3g-3j in DMF

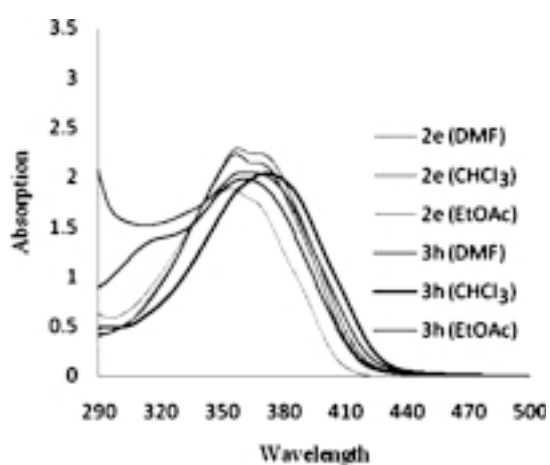


Fig. 3: Absorption spectra of compound 2e and 3h in different solvents

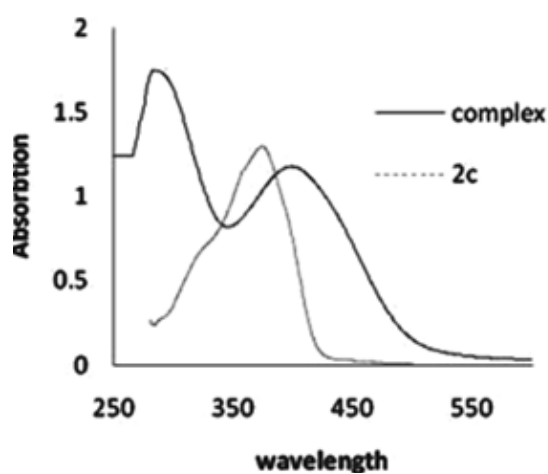
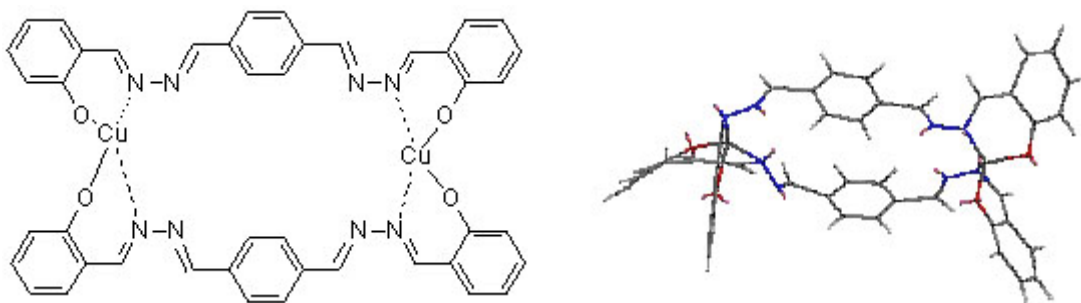


Fig. 4: UV-Vis spectra of the Schiff base ligand 2c and its complex 4

The UV-Vis spectra of the complex **4** shows intense band in the range of 398.5, 310 and 330 nm relative to that of initial **2c** ligand 375.2 nm .

This different absorption behavior is assigned to the  $\pi \rightarrow \pi^*$  charge transfer band gap for complex **4** (Fig. 4).



Scheme 3: MM2 model of **4** shows [7,7] paracyclophane

#### ACKNOWLEDGMENTS

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